



Effects of temperature and rich-phase composition on the performance of a commercial NO_x-Storage-Reduction material



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ABSTRACT

A thin self-supported wafer of a commercial NO_x-Storage-Reduction (NSR) material was investigated by *operando* transmission FT-IR to assess the effects of the operating temperature and the composition of the rich period (in particular with respect to H₂, CH₄, CO, CO₂ and C₃H₆ reactants) on the deNO_x activity. The DeNO_x activity was high at 300 °C under the simulated exhaust gas composition, but dropped sharply at 200 °C and 100 °C, primarily due to a loss of the NO_x storage ability. The origin of the trapping loss depended on the temperature. Pt-bound CO(ads) were observed at 200 °C, pointing to a significant poisoning of metallic Pt sites by strongly bound carbon monoxide, hindering NO_x decomposition and reduction. Surprisingly, no Pt-CO was observed at 100 °C, revealing the absence of accessible metallic Pt at this temperature, most likely due to the presence of a fully oxidized (or nitrated) Pt surface. In contrast, an important NSR activity could be obtained at 200 °C and even at 100 °C when H₂ was used as the only reducing agent in a C-free feed. Propene had a similar detrimental effect as that of CO, while methane only induced a minor loss of trapping efficiency. The presence of a large concentration of CO₂ also induced a trapping loss, albeit significantly less marked than those due to propene and CO. The combination of all the C-containing compounds (i.e. CO, CO₂, C₃H₆, CH₄) led to an almost complete inhibition of the NSR activity at temperatures equal to or lower than 200 °C. The *operando* analysis also revealed that the nature of the NO_x species trapped varied with the temperature; nitrates were the dominant species at 300 °C, while nitrites were more prominent at 200 °C and 100 °C.

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1. Introduction

The NO_x-Storage-Reduction (NSR) technique has been introduced by Toyota to treat the NO_x emissions of lean-burn engines, which offer important fuel savings and decrease CO₂ emissions as compared to stoichiometric engines [1,2]. A description of the NSR technique and a review of the activity of many materials have been reported elsewhere [3]. The understanding of NSR technology has been hampered by the fact that various (usually non-realistic) reaction conditions were often used and a very large number of model materials with varying formulations were investigated [4–22].

Several studies have been devoted to commercial NSR materials [23–26] and *in situ* FTIR studies [27–30], but rarely the combination of the two has been reported. One of the difficulties associated with

commercial samples is the large number of components present, making difficult the interpretation of *in situ/operando* IR spectra. In an earlier paper [31], we showed how the simultaneous combination of *operando* spectroscopic FTIR data and kinetics enabled unravelling important features of the activity of a commercial NSR material.

While both covalent (i.e. surface) and ionic species were observed, the large NO_x uptake observed during NSR operation at 300 °C could be mostly related to the replacement of ionic-like carbonates by ionic-like nitrates, probably only in a barium carbonate phase [31]. The sites in the bulk of large barium carbonate particles were yet proposed not to be taking part in the storage. The contribution of covalent species (e.g. formed on surface sites of alumina and ceria) to storage at 300 °C was negligible, although some of those species may serve as transport intermediates in the formation of ionic species.

The present work aims at investigating the effect of the operating temperature and the composition of the reduction feed on

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Table 1

Concentrations of gases in the base, rich and lean feeds during various types of NSR experiments, which consisted of a succession of exposure for 10 min to the (base + lean) feeds followed by 30 s of exposure to the (base + rich) feeds.

	Standard	C-free	H ₂ -C ₃ H ₆	H ₂ -CH ₄	CO-H ₂	H ₂ -CO ₂
Base feed (always present)						
H ₂ O	4%	4%	4%	4%	4%	4%
CO ₂	10%	–	–	–	–	10%
Rich feed						
CO+H ₂ (3:1)	2.89%	–	–	–	9%	–
H ₂	–	9%	3.6%	8.3%	–	9%
C ₃ H ₆	0.58%	–	0.58 %	–	–	–
CH ₄	750 ppm	–	–	750 ppm	–	–
O ₂	0.89%	0.89%	0.89%	0.89%	0.89%	0.89%
Lean feed						
O ₂	8.7%	8.7%	8.7%	8.7%	8.7%	8.7%
NO	140 ppm	140 ppm	140 ppm	140 ppm	140 ppm	140 ppm

the NSR activity of the same commercial catalyst. The combination of *operando* spectroscopic FTIR and kinetic data will enable determining directly some of the reasons for the loss of NSR activity at temperatures lower than 300 °C.

2. Experimental section

A powder of the NSR material was detached from an oven-aged cordierite-based monolith supplied by Renault SAS using an undisclosed method. The exact composition of the powder cannot be disclosed but Pt was the main noble metal (ca. 0.6 ± 0.5 wt.%), followed by Pd (ca. 0.2 ± 0.1 wt.%) and then Rh (ca. 0.1 ± 0.05 wt.%). As far as oxides were concerned, the main constituents were the following, in order of decreasing concentration: Al (ca. 25 ± 5 wt.%), Ce (ca. 15 ± 5 wt.%), Si (ca. 7 ± 3 wt.%), Mg (ca. 7 ± 3 wt.%), Ba (ca. 4 ± 2 wt.%), Zr (ca. 2 ± 1 wt.%), Fe (ca. 0.6 ± 0.4 wt.%), Sr (ca. 500 ± 300 wt. ppm) and Cs (ca. 700 ± 300 wt. ppm).

The experimental procedures are given in details elsewhere [31]. In brief, a transmission FTIR *operando* cell fitted with KBr windows was used for the analysis of the catalyst surface, while a mass spectrometer was used to monitor the cell effluent. A chemiluminescence cell (From ThermoScience, model 42i-HL) was also used for some experiments to precisely determine NO and NO₂ concentrations at the exit of the reaction cell. The samples were pressed into self-supporting wafers of about 10 mg cm⁻².

Feed conditions representative of those occurring in NOx trap converters dedicated to treating the emissions of a Euro 4 Diesel engine were used for the lean and rich phases. The compositions are given in Table 1 indicating that the lean phase exhibited a large O₂ excess. The so-called “base” feed was always present in the feed sent to the reaction cell. The NSR cycles consisted of a succession of exposure for 10 min to the (base + lean) feed followed by 30 s of exposure to the (base + rich) feed.

The total flow rate passing over the wafer was 25 ml/min. Note that the lean and the rich phase feeds were merged after the reaction cell and simultaneously analysed, so that any NOx released during the rich phase could also be measured. Before applying the cycling NSR procedure, the sample was activated at 600 °C under the (standard rich + base) feed for one hour and then the temperature was set to that of the experiment.

Non-standard rich feed were also used to investigate the individual effects of each of the reactants (Table 1). In such cases, all carbon-containing species were removed from the reduction feed after 30 min, allowing the sample to be activated only under H₂ (using the “C-free” feed) for another 30 min. A computer-controlled automated 6-way valve (Swagelok) was used to switch either the lean or rich feed to the reaction cell in addition to the base feed. The NSR material was typically stabilized over five full cycles before five

other cycles were collected to calculate an averaged NSR activity. The NOx conversion is defined by the equation:

$$\text{NOx conversion} = \frac{\text{NO fed} - \text{NOx measured}}{\text{NO fed}} \quad (1)$$

where NO fed is the amount of NO introduced to the reactor over a full cycle and NOx measured is the amount of NOx (=NO + NO₂) measured also over a full cycle. The maximum theoretical conversion was ca. 95 %, because of the way the experiment was designed: the stream containing NO by-passed the reactor for 30 s over a total cycling period of 10.5 min. The nature of the reduction products was not investigated in details, but gas-phase IR analysis revealed significant proportions of N₂O, while ammonia was not observed (N₂ is not IR sensitive and cannot be resolved by MS studies in the presence of large concentrations of CO and CO₂). The fraction of NOx trapped over the lean period was also calculated using the same equation as that for the NOx conversion but only taking into account the NO fed and NOx in the cell effluent during the lean period:

$$\text{NOx trapped} = \frac{\text{NO fed(lean)} - \text{NOx measured(lean)}}{\text{NO fed(lean)}} \quad (2)$$

Note that the value of NOx trapped was usually greater than that of NOx conversion because not all the NOx trapped were reduced during the rich phase.

3. Results and discussion

3.1. Effect of the operating temperature

The NSR activity of the commercial material in terms of NOx trapping (Fig. 1a) and NOx conversion (Fig. 1b) was measured at three different temperatures for a dry feed and for a wet feed in which 4 vol.% water was present (i.e. standard NSR feed, as given in Table 1). The NSR material was functioning at 300 °C and minor losses of NOx trapping and conversion were observed in the case of the wet feed as compared to the dry case. The value of NOx conversion was always lower than that of NOx trapping, indicating that not all of the NOx trapped were eventually reduced.

The activity of the NSR material dropped dramatically when the temperature was set at 200 and 100 °C (Fig. 1) under both dry and wet feed. The NOx conversion was essentially nil, mostly due to the fact that the level of trapping has dropped to about 5% at 200 °C and was essentially nil at 100 °C. Since the activity observed under the dry and wet feed were similar, only the case of the dry feed are further detailed in this section for the sake of simplicity.

The absorbance IR spectra of the NSR material obtained at the three different temperatures (under the rich+base feed) following activation were essentially identical (Fig. 2). Note that the large bands due to gas-phase CO₂ were mostly due to the CO₂(g) present

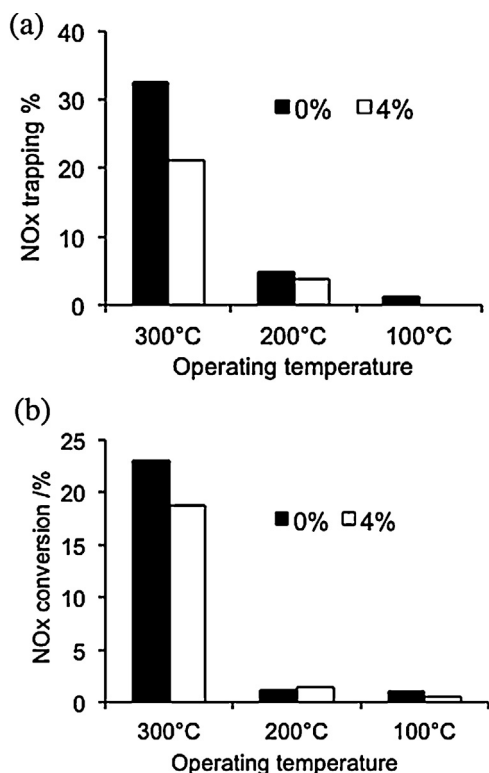


Fig. 1. Effect of the operating temperature on the (a) proportion of NOx stored and (b) NOx conversion. Two concentrations of added water were used: 0 and 4 vol.%. The concentrations of other gases were that of the standard NSR feed (see Table 1).

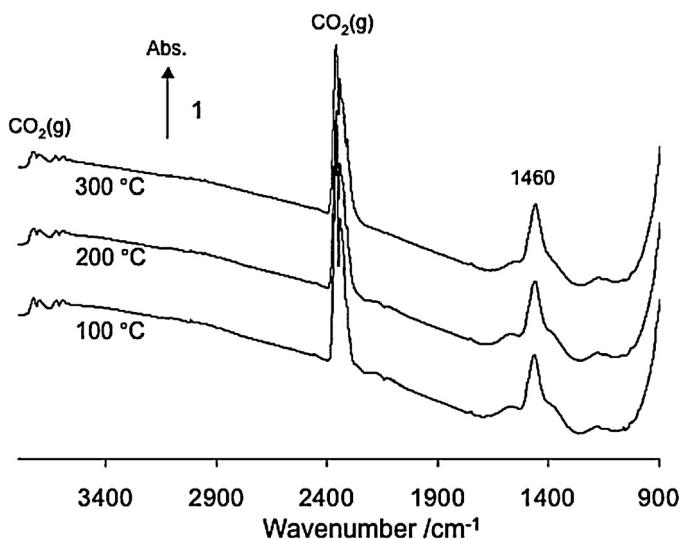


Fig. 2. FTIR operando spectra obtained over the activated commercial NSR material at 100, 200 and 300°C after activation (no water added). A spectrum obtained with the empty IR cell was used as background to calculate the absorbance.

in the cell dead-volume (albeit small) around the wafer. A major absorption band was noted at 1460 cm⁻¹, corresponding mostly to barium carbonates [32,33]. Several other bands or shoulders were observed around this main peak, due to surface and bulk carbonates (discussed in reference [31]) over the many other oxides present in the commercial sample. No band decomposition or precise assignment of this region was attempted because of the large number of peaks expected.

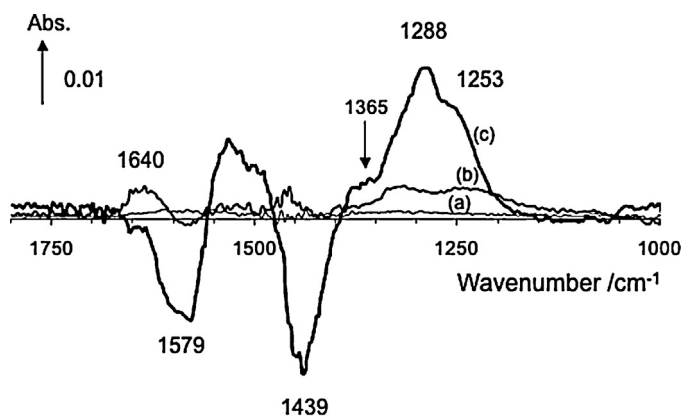


Fig. 3. FTIR operando spectra obtained over the activated commercial NSR material at 100°C (a, thin line), 200°C (b) and 300°C (c, thick line) at the end of the lean phase feed (no water added). A spectrum obtained over the same sample at the same temperature at the beginning of the lean phase was used as background to calculate the absorbance.

The variation of the *in situ* IR spectrum measured over the sample during the lean phase was investigated with a view at understanding NOx adsorption at the three temperatures of interest. The absorbance spectra presented in Fig. 3 were calculated using the difference between the final spectrum of the lean-phase as sample signal and the one at the beginning of the lean phase as reference signal [34]. Therefore, these spectra should represent the combination of species that were formed (displaying a positive absorbance) and removed (displaying a negative absorbance) during the lean period.

The description of the spectrum obtained at 300°C has already been reported elsewhere [31], but it is briefly recalled here. The 1288 and 1253 cm⁻¹ bands are assigned to the asymmetric stretching vibration of covalent (or surface) NOx species; the high frequency counterpart being around 1500 cm⁻¹ region, which is mostly cancelled out by a negative carbonate signal (Fig. 3). The most important species for adsorption were shown to be ionic nitrates [31], the band of which is located at ca. 1365 cm⁻¹, partly overlapping with that of bulk ionic carbonates. The negative bands at 1439 and 1579 cm⁻¹ are mostly due to bulk and covalent/surface carbonates.

The spectrum obtained at 200°C was much flatter and no removal of carbonates was observed. The weak bands observed were possibly due to nitrite species (1320, 1250 cm⁻¹) and molecular water (1640 cm⁻¹) formed from H₂ combustion during the previous rich period. The spectrum obtained at 100°C was essentially featureless, stressing that neither adsorption nor desorption were taking place during the lean-phase. These IR data are consistent with the gas phase analysis (Fig. 1a) that showed that the NOx trapping efficiency was close to zero at 200°C and 100°C.

The FTIR spectra recorded at the three studied temperatures in the wavenumber region corresponding to the absorption of gas-phase CO and CO(ads) are shown over a period of about 12 min, which included two rich periods and one lean period (Fig. 4). No CO(g) nor any carbonyl species could be observed at anytime at 300°C, indicating that essentially all of the CO introduced during the rich phased was converted.

In contrast, a large band of CO(g) (showing the P and R branches of the rovibrational spectrum) were observed both at 100 and 200°C. This observation is consistent with the fact that no NOx reduction activity was observed at these low temperatures and that the CO present during the rich periods was not fully oxidized.

In addition, an intense carbonyl band located at ca. 2075 cm⁻¹ was observed at 200°C during the rich phase (Fig. 4, middle spectra). The observation of a carbonyl band indicates that the metallic

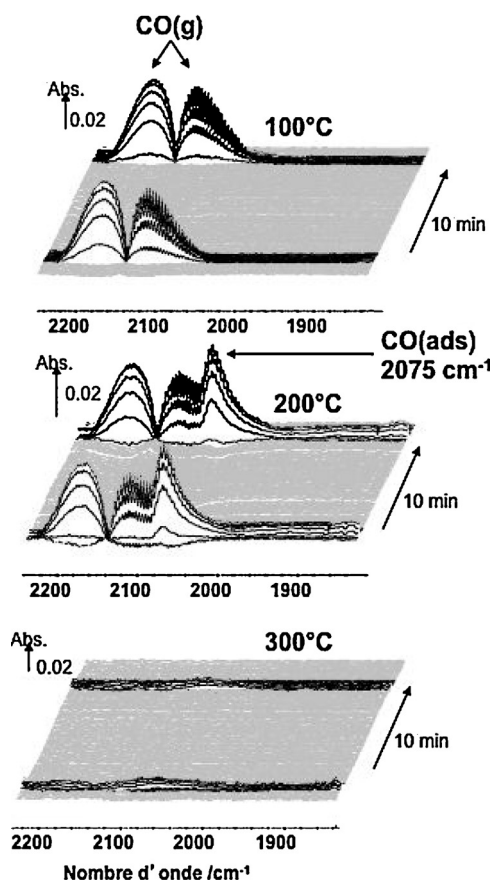


Fig. 4. FTIR *operando* spectra showing the CO(ads) stretching region recorded over the activated commercial NSR material at 100, 200 and 300 °C over a duration of ca. 12 min including two rich periods (black lines) and one lean period (grey lines). The lean period is indicated by the 10 min arrow. A spectrum obtained over the same sample at the same temperature at the beginning of the lean phase was used as background to calculate the absorbance.

Table 2

Concentration of NO and NO₂ measured by chemiluminescence at the cell exit measured at the end of the lean period. Operating temperature = 200 °C, no added water.

	NO(ppm)	NO ₂ (ppm)
C-free feed	77	28
Standard feed	107	27

sites (mostly Pt) were covered, at least in part, with CO, the adsorption enthalpy of which is high, typically between 85 kJ/mol (at full coverage) to 180 kJ/mol (at zero-coverage) for alumina-supported Pt [35].

It is therefore possible that at 200 °C many, if not all, metallic sites were poisoned by CO during the rich phase and explain the lack of overall NSR activity due to a lack of reduction of adsorbed NO_x species. In stabilized cycles at 200 °C, only little NO_x species adsorbed during the lean phase (Fig. 1a, likely because sorption sites were occupied) and those were hardly reduced during the rich phase (Fig. 1b). It must be noted that the NO to NO₂ oxidation ability of the sample during the lean-phase was not changed at 200 °C (Table 2).

The fact that carbonyl species were not observed at 100 °C in the presence of gas-phase CO indicates that no accessible Pt metallic sites were available. The most likely origin of this fact is that the surface (or even bulk) of the metal particles were oxidised, making CO adsorption unfavourable. The loss of NSR activity at 100 °C would thus be due to the lack of regeneration of the storage sites.

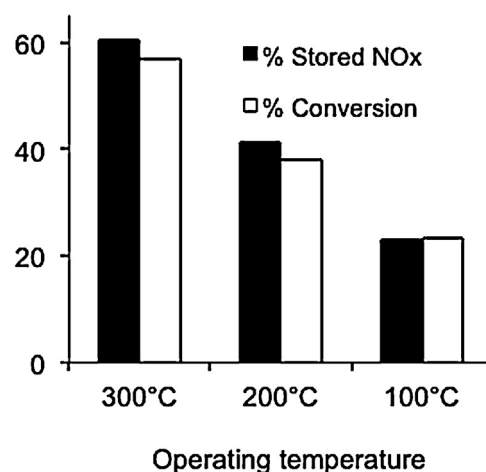


Fig. 5. Effect of NSR operating temperature on NO_x trapping and NO_x conversion at various temperatures in the absence of any C-containing molecules. 4% water added.

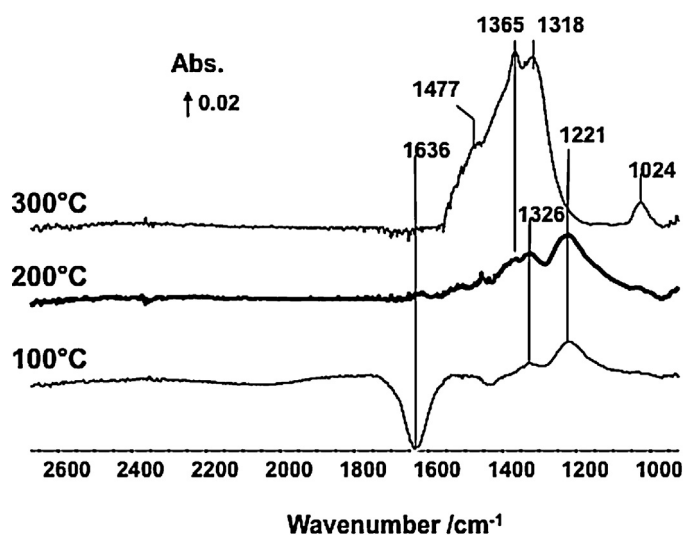


Fig. 6. *Operando* FTIR spectra obtained over the activated commercial NSR material at 100, 200, and 300 °C under the lean phase feed comprising 4% water concentration in the absence of carbon-containing molecules in the feed. A spectrum obtained over the same sample at the same temperature at the beginning of the lean phase was used as background to calculate the absorbance.

3.2. Effect of the rich feed composition

Since poisoning of the metal by CO during the rich phase was suggested as a possible cause for the loss of NSR activity at 200 °C, the activity of the commercial material was investigated using a feed free of carbon-containing molecules. The concentration of H₂ in the rich phase was increased to keep unchanged the stoichiometric reducing potential (see Table 1, compare “C-free” column to that labelled “standard”). CO₂ also had to be removed from the lean-period, because it can be readily reduced to CO over Pt-based catalysts through the reverse water-gas shift reaction [36].

The NO_x-storage ability and NSR activity under a C-free feed (Fig. 5) were markedly higher than those obtained in the case of the standard feed (Fig. 1). Most interestingly, the NSR commercial material still exhibited a marked conversion at 200 °C and even at 100 °C (Fig. 5).

The variation of the IR signal between the beginning and the end of the lean-phase in the case of the C-free feed was recorded at the three temperatures of interest (Fig. 6). The nature of the sorbed NO_x species during the lean-phase clearly depended on the tem-

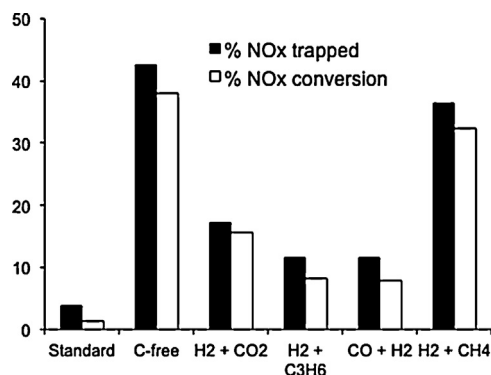


Fig. 7. Effect of the composition of the NSR rich feed on NO_x trapping and NO_x conversion at 200 °C (4% of added water was present).

perature. A broad composite band was observed at 300 °C centred at ca. 1365 cm⁻¹, which was consistent with the presence of ionic (D_{3h}) nitrates, most likely barium nitrate species. Other NO_x(ads) species were also present (e.g. shoulders at 1477, 1318, 1024 cm⁻¹) and likely corresponded to covalent surface species adsorbed on the various oxides present [37,38].

The spectra obtained at 200 °C and 100 °C were quite different from that measured at 300 °C. The main IR bands were located at ca. 1221 and 1326 cm⁻¹, likely due to various nitrite species [33,39,40,41]. The band around 1365 cm⁻¹ was hardly visible at the lower temperatures, suggesting that nitrites oxidation to nitrates was limited. A strong negative band at 1636 cm⁻¹ was noted at 100 °C, which is assigned to adsorbed molecular water. This water (in excess to the 4% already fed) was formed during the rich phase by oxidation of H₂ and was able to adsorb in significant quantities because of the low reaction temperature, before gradually desorbing during the lean phase.

While it is clear that using a C-free feed led to a dramatic increase of the NSR activity of this commercial material, especially at the lowest temperatures (Fig. 5), the experiments reported above do not enable determining conclusively what was(were) the compound(s) responsible for the low activity observed with the standard feed. Therefore, a series of experiment was carried out at 200 °C in which each of the C-containing molecules was individually added along with H₂ in the rich feed, keeping the overall reducing power constant on a stoichiometric point of view. The details of the feed are given in Table 1. One experiment was also done in which 10% of CO₂ was added to both rich and lean-phase, H₂ remaining the only reducing agent in the rich phase.

The results (Fig. 7) show that at 200 °C all molecules (i.e. CO₂, C₃H₆, CO) led to a significant decrease of the NO_x trapping efficiency and consequently the NO_x reduction, except for methane, for which the loss was minor. The activity observed in the case of the CO₂, C₃H₆, CO-containing feeds was yet still higher than that measured in the case of the standard feed, indicating that the role of each molecule was different and that the combination of those synergistically limited the NSR activity.

The corresponding *in situ* FTIR spectra in the C–O stretching region (Fig. 8) were different from those recorded under the standard feed at the same temperature of 200 °C (Fig. 4). In the cases of the feeds containing propene or CO₂, no gas-phase CO nor carbonyl species could be detected in the rich phase. This indicates that poisoning of the metallic sites by CO was not the main origin of the NSR activity loss in these cases. CO(g) and carbonyl species at around 2060 cm⁻¹ were observed in the case of the CO-containing feed, as expected. Note that the band intensities were different from those reported in Fig. 1, primarily because the actual CO concentration was about 6.8%, instead of 2.2% in the standard feed (Table 1) to keep the overall reducing power.

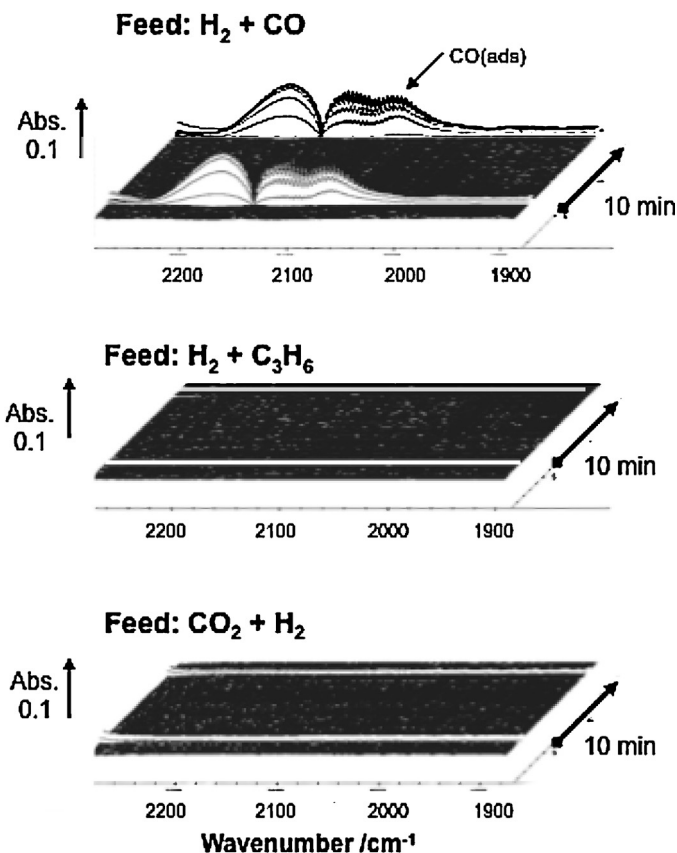


Fig. 8. FTIR *operando* spectra in the C–O stretching region recorded over the commercial NSR material at 200 °C over a duration comprising two full rich periods and one full lean period. The lean period is indicated by the 10 min arrows. Top spectra: the rich phase contained H₂ and CO. Middle spectra: the rich phase contained H₂ and propene. Bottom spectra: the rich phase only contained H₂, but CO₂ was present in both lean and rich phases. See Table 1 for exact feed composition. A spectrum obtained at the beginning of the lean phase was used as background to calculate the absorbance.

The *in situ* FTIR spectra in the 2000–1000 cm⁻¹ region showing the variation of signal over the lean period also revealed marked differences between the various feeds (Fig. 9). The IR spectrum for the H₂ + CH₄ was similar to that of the C-free experiment. The nitrite band at 1223 cm⁻¹ was of similar intensity, while the nitrate band at 1365 cm⁻¹ was somewhat decreased for the H₂ + CH₄ experiment.

The feeds related to propene, CO and CO₂ all resulted in a much weaker nitrite signal, as expected from the lower storage efficiency observed in these cases (Fig. 7) and in agreement with previous studies with previous studies [42]. The formation of carbonates species (that desorbed during the lean period, leading to negative bands) occurred under these conditions, hence it is difficult to draw any conclusion on the intensity of the bands in the 1600–1200 cm⁻¹ region. Nonetheless, no nitrate band was visible and the intensity of the nitrite band was the lowest in the case of the CO₂-containing feed, while the corresponding NO_x storage percentage was actually higher than those measured in the case of the CO and propene-containing feeds (Fig. 7).

It must be noted that in the case of the CO₂-containing feed, 10% of CO₂ was present both in the lean and rich period and therefore the relative carbonate signal change was low over the lean period. On the contrary, carbonates could only form from CO and propene oxidation during the rich period in the case of the corresponding feeds, yielding a more marked relative change. In conclusion, no fully quantitative comparison of signal change can be obtained from this region.

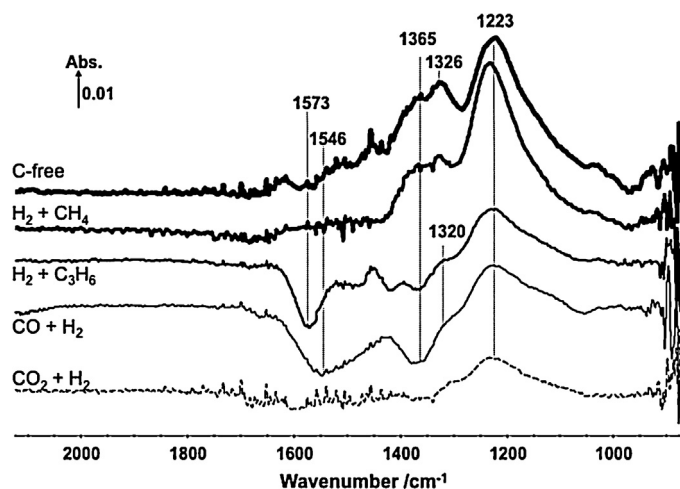


Fig. 9. FTIR *operando* spectra obtained over the activated commercial NSR material at 200 °C under the lean phase feed comprising 4% water concentration. Each spectrum is labelled according to the name of the compound present during the rich phase along H₂ (see Table 1 for exact feed composition). A spectrum obtained at the beginning of the lean phase was used as background to calculate the absorbance.

A rather sharp band was observed at 1573 cm⁻¹ in the case of the propene-containing feed. No such band was ever observed under standard conditions or experiment involving surface titration with CO₂. It is therefore unlikely that this band related to a surface carbonate species. Alkenes can readily decompose to cationic allylic species on acidic sites, which lead to a strong band at around 1575 cm⁻¹ [43,44]. The (oxi) dehydrogenation and aromatisation of propene catalysed by the metals present could be envisaged and would lead to bands in the same region. This band could also correspond to acetate species as reported in a recent study involving decane as another reducing agent [45]. While more work would be needed to ascertain the nature of the 1573 cm⁻¹ band observed here, it probably related to a propene-derived compound that directly induced some deactivation of the NSR activity. This work stresses that propene is clearly not an ideal reducing agent for the NSR technology, while it is usually a reducing agent of choice for the selective catalytic reduction of NO_x (which continuously operates in lean conditions) over similar catalysts [46].

3.3. On the relevance of species detected by IR during *operando* studies

In a previous paper [31], we have hypothesized that the NO_x species of importance for the NSR activity over this commercial material were ionic nitrates, which were essentially not directly visible on the IR spectra reported in this earlier paper. This conclusion could yet be drawn thanks to a rigorous mathematical analysis of the variations of intensity in the related spectral regions during the lean period [31].

The use of a C-free feed in the present report enabled us eventually observing directly these ionic nitrates, located at around 1365 cm⁻¹ (Fig. 6). The IR spectra of the species that built up during the lean-phase at 300 °C using a normal feed and using a C-free feed are shown in Fig. 10. At this temperature, the material was active under both feeds and the NO_x storage was 90 μmol g⁻¹ for the C-free feed and 25 μmol g⁻¹ for the standard feed, hence a ratio of ca. 3.6 between the two storage capacities.

However, the comparison of the two spectra (Fig. 10) indicates that the intensity of the observed NO_x band (centred at 1365 cm⁻¹) in the C-free case was far greater than 3.6-fold that observed in the case of the standard feed (centred at 1288 cm⁻¹). The bands

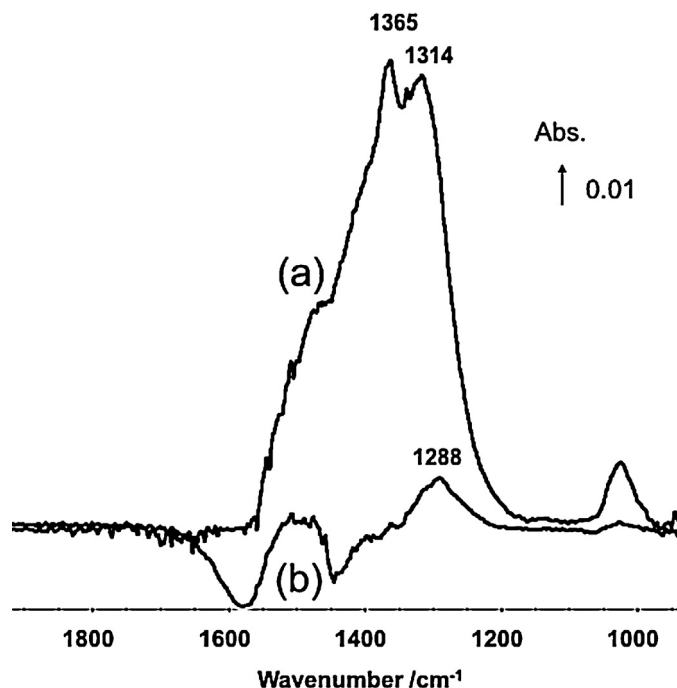


Fig. 10. FTIR *operando* spectra obtained over the activated commercial NSR material at 300 °C under the lean phase feed comprising 4% water concentration (a) with the C-free feed and (b) with the standard feed. A spectrum obtained over the same sample at the same temperature at the beginning of the lean phase was used as background to calculate the absorbance.

appeared also at different positions. These apparent mismatches were due to the overlap between the negative carbonate bands and positive NO_x bands, which only makes visible the covalent NO_x at ca. 1288 cm⁻¹ [31]. Furthermore, it is also obvious from Fig. 10 that carboxylate or acetate species (negative bands at ca. 1575 and 1450 cm⁻¹) competed with nitrates for adsorption under the standard feed at 300 °C.

This comparison highlights an interesting paradox. In the case of the standard feed, the signal of the main species of interest (centred at 1365 cm⁻¹) was completely masked by that of disappearing carbonates, while the only visible NO_x species (covalent NO_x at 1288 cm⁻¹) has a rather unimportant contribution to the NSR process [31]. It is yet another example of *operando* spectroscopic studies during which the species that can be monitored actually do not contribute significantly to the catalytic/NSR process, while the important ones remain “invisible” at the first look. Other examples of the irrelevance of species observable by *operando* IR regard, for instance, formates “seen by IR” during the water-gas shift reaction [47–49]. Only thorough spectrokinetic analyses, supported by complementary tests in transient conditions can distinguish active species from spectators [50,51,52].

4. Discussion

The activity of a commercial NSR material using a representative standard feed (Table 1) exhibited an almost complete loss of storage ability, thereby inducing a similar loss of NO_x reduction, when the temperature of operation was reduced from 300 °C down to 200 or 100 °C (Fig. 1).

Improved NO_x storage and reduction could be obtained, especially at 200 or 100 °C, when removing any carbon-containing molecules from the feed (Fig. 5). These C-free experiments enabled a direct observation of the nature of the stored NO_x (Fig. 6), as no carbonates were interfering with the NO_x sorption. Interestingly,

the nature of the trapped NO_x changed with the temperature. Ionic nitrates were observed at 300 °C, while mostly nitrites species were present at 100 and 200 °C. This observation is in agreement with work realized on model Pt-Ba-alumina materials by Ji et al. [28] and Lietti et al. [53,54], who concluded that nitrates were prevalent above 300 °C and nitrite below this temperature. NSR experiments also carried out over a model Pt-Ba/alumina materials using various H₂ concentrations concluded that the best efficiency was obtained at 270 °C and 1% H₂ [55]. Ammonia has been reported as an important intermediate in the reduction of NO_x. In the present case, ammonia was never observed, possibly because its concentration was below the detection limit of our gas-cell and it readily reacted with NO_x to yield N₂ and N₂O.

Note that the oxidation rate of NO to NO₂ was not modified at 200 °C in the presence of the C-containing molecules (Table 2) and therefore this step can be excluded as the one responsible for the loss of activity.

Since in all cases the fraction of NO_x reduced was almost identical (more precisely, slightly lower) to that of stored NO_x (see Figs. 1, 5 and 7), it can be concluded that the main limiting factor in NSR activity of this commercial sample is the ability to store NO_x. A series of experiments were conducted varying the composition of the rich feed and CO₂ concentration to try to identify the molecules responsible for the deactivation at low temperatures (Table 1). All the carbon molecules were shown to lead to a significant NO_x trapping loss, except for methane, which is expected because of the relative inertness of this molecule at low temperatures (Fig. 7).

No single origin for the reduction in NO_x trapped could be evidenced. The gas phase data (Fig. 7) and *operando* IR data (Figs. 3, 4, 8 and 9) suggested that the cause for the marked deactivation of the NO_x trapping efficiency was multiple and related to the various molecules as follow:

- i.) in part due to the adsorption competition with CO₂ for the surface/bulk basic sites.
- ii.) in part due to the formation of a propene-derived adsorbates (possibly an allyl or acetate species), poisoning metallic and/or oxide surface sites.
- iii.) in part due to the poisoning of the metallic sites with CO, which affected the regeneration of the trap (lower exotherm provided for full nitrate or nitrite decomposition to gas-phase NO_x and subsequent reduction), but not the oxidation of NO to NO₂ (Table 2).

Note that our results on the detrimental role of CO at low temperatures are in agreement with those of Al-Harbi and Epling [24] obtained on model and commercial NSR materials. Ji et al. [28] and Breen et al. [9] also noted that H₂ was a better reducing agent than a mixture of H₂ and CO, particularly at low temperatures. Breen et al. [9] proposed that the main effect of CO was Pt poisoning by strongly bound carbonyls. In addition to Pt poisoning, Ji et al. [28] also proposed that the oxidation of CO to CO₂ during the rich phase resulted in the formation of a layer of carbonate that inhibited the NO_x decomposition. It is likely that the deactivating effect of CO is diverse and depends on the experimental conditions, in particular depending on the occurrence of the water-gas shift reaction, which favours CO removal from metal surfaces as noted by Ji et al. [28].

Note that the NO_x reduction ability of our commercial sample was also somewhat affected by the C-containing reducing agent, as a significant proportion of the stored NO_x was not reduced at 200 °C in the case of the standard feed (Fig. 1). However, the most important factor contributing to the overall loss of NSR activity was clearly the loss of trapping ability, likely due to hindered trap regeneration [7,28].

5. Conclusions

The *operando* IR data reported here show that the nature of NO_x stored on a commercial sample varied with temperature: ionic nitrates were observed at 300 °C, while mostly nitrites species were present at 100 and 200 °C. An almost complete loss of NSR activity was observed at 200 and 100 °C, due essentially to the loss of trapping ability. Pt-bound CO(ads) were observed at 200 °C under rich conditions, pointing to a significant poisoning of metallic Pt sites by strongly bound carbon monoxide. The surface of the noble metals (mostly Pt) was fully oxidized at 100 °C, even under the rich phase. The use of C-free feed enabled obtaining significant NSR activity at 200 °C and even at 100 °C. Each of the other C-containing reductants and molecules, i.e. CO, propene, CH₄ and CO₂, has a detrimental effect on the NSR activity, which is completely inhibited at low temperatures (≤200 °C) when these effects are combined.

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